

**CATALYST BASED ON FERRIERITE/IRON FOR CATALYTIC
REDUCTION OF NITROUS OXIDE CONTENT IN GASES, METHOD FOR
OBTAINING SAME AND APPLICATION**

Cross-referenced and Related Applications

[001] This application is a divisional of U.S. application 09/582,622 which was filed on June 20, 2000 which was a 371 of PCT/FR98/02747 filed December 16, 1998 which claimed priority to FR97/16803 filed on December 31, 1997 which are hereby incorporated by reference in their entirety.

Background of the Invention

(i) Field of the invention

[002] The invention comes within the general scope of the reduction of the content of greenhouse gases in gaseous effluents of industrial origin discharged to the atmosphere. It is a question here of lowering nitrous oxide N_2O in gaseous discharges.

[003] For a long time, concern was only felt about the discharge of nitric oxides (NO_x), which easily combine with water to form nitrous or nitric acids, the most spectacular sign of which is without doubt acid rain, with subsequent destruction of forests and damage to exposed monuments, and the most insidious signs of which are contamination of breathable air and its effect on public health. Awareness has now arisen of the significant contribution of nitrous oxide to enhancing the greenhouse effect, with the risk of leading to climatic changes with uncontrolled effects, and perhaps also of its participation in the destruction of the ozone layer. Its removal has thus become a preoccupation of the authorities and of manufacturers.

[004] While the most significant sources of N_2O are the oceans, uncultivated soils, agriculture, the combustion of organic matter and the use of fossil fuels, the chemical industry contributes some 5 to 10% of emissions of this gas. Nitric acid plants, as well as plants for organic synthesis employing nitric oxidation processes (production of adipic acid, of glyoxal, and the like), are the source of most discharges of N_2O by the chemical industry (see, in this respect, Freek Kapteijn et al., Heterogenous Catalytic Decomposition of Nitrous Oxide, in Applied Catalysis B, Environmental 9, 1996, 25-64).

[005] For some years already, most nitric acid plants have been equipped with so-called DeNO_x reactors, which operate satisfactorily in removing nitric oxides from their effluents. However, N₂O which is essentially produced during the oxidation of ammonia over the platinum gauzes of the burners, remains substantially constant between the outlet of the burners and the inlet of the DeNO_x reactor and is not lowered by passage of the gases through this reactor (sometimes, it is even slightly increased).

[006] Provision has been made to reduce the N₂O content of the gaseous effluents resulting from nitric oxidation processes in organic chemistry by catalytically destroying the nitrous oxide contained in the latter over a mordenite/iron catalyst (EP 0,625,369). However, on account of the large fall in its activity in the presence of steam in the temperature range 350-450°C, this catalyst is not well suited to functioning with respect to dilute gases and ages badly, due to a mediocre hydrothermal resistance.

[007] It also turns out to be economically unsuited to the treatment of the tail gases from nitric acid plants, which, upstream of the expansion turbine, generally correspond to the following characteristics,

- temperature: < 400°C
- N₂O content: between 500 and 1500 ppmv,
- NO_x content: between 50 and 2000 ppmv,
- H₂O content: between 0.5 and 5%.

[008] The economic optimization of the lowering of N₂O both in the gases emitted by organic plants and by nitric acid plants involves the development of a catalyst which retains a good activity for the destruction of N₂O at a temperature below 400°C in the presence of NO_x and of steam, and which has a sufficient hydrothermal stability at 600°C to withstand the temperature peaks to which it may be subjected under certain circumstances in its use.

(ii) Description of Related Art

[009] A solution corresponding to such specifications has just been found with a catalyst composed of agglomerates formed of 80 to 90% of a ferrierite/iron assaying from 1 to 6% of iron, and preferably from 2 to 4%, and of 20 to 10% by weight of an agglomeration binder (percentages by weight with respect to the weight of the granule).

Summary of the Invention

[010] The ferrierite/iron is the active component of the catalyst according to the invention. The structure of its crystal lattice is that of ferrierite [RN = 12173-30-7], that is to say a zeolite traversed by two systems of channels, one parallel to the c axis of the structure, formed of channels with an elliptical cross-section (0.43 nm x 0.55 nm) of approximately 0.18 nm^2 (18 \AA^2), the other parallel to the b axis and the c axis of the structure, with channels formed of 8-membered rings, with 0.34 x 0.48 nm axes. There is no channel parallel to the a axis. Approximately spherical cavities, with an approximate diameter of 0.7 nm, lie on these channels and are accessible only through the 8-membered rings, i.e. via 0.43 nm x 0.55 nm or 0.34 nm x 0.48 nm pores. The ferrieritic structure is completely characterized by its X-ray diffraction diagram (for the interlattice distances, consult Breck "The Synthetic Zeolites", 1974 Edition, Table 4.45, p. 358).

[011] This ferrierite/iron is obtained by subjecting a commercial ferrierite, of sodium/potassium type, to exchange with an aqueous solution of an iron salt, so as to obtain the desired iron content. The operating procedures are well known to a person skilled in the art. It is possible, in particular, to carry out one or more exchanges by immersion in an iron salt solution or by column percolation, either of the ferrierite powder itself or with respect to granules.

[012] This exchange can be carried out either using a ferric salt solution or using a ferrous salt solution. Use is advantageously made of ferrous sulphate, which is a very low cost product and which does not introduce chlorides, which are sources of corrosion, into the preparation.

[013] Preference is given to the form exchanged with iron starting from the ammonium form of ferrierite, which is obtained by subjecting a commercial ferrierite, the electrical neutrality of the crystallographic lattice of which is essentially produced by sodium and potassium alkali metal ions, to an exchange with a solution of an ammonium salt. The ferrierite/iron obtained from the ammonium form of ferrierite exhibits, as characteristic, that of having a very low content of alkali metal ions in the exchange position. It is the low content of potassium ions (less than 0.5% by weight) which analytically indicates this preferred form of the catalyst of the invention. The ferrierites/iron according to the invention contain only 0.5 to 0.1% of potassium.

[014] The catalysts according to the invention are shaped as agglomerates, a presentation which is necessary for reasons of minimization of the pressure drop as they pass through the catalyst bed. The agglomeration of zeolites is well known to a person skilled in the art. It is carried out

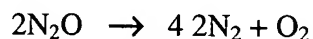
by forming a paste of the zeolite powder with a binder, generally fluidified with water, often composed of a clay which is simultaneously sufficiently plastic to be able to form the agglomerate as balls, using a dish granulator, as pellets by molding or as extrudates, using an extruder, and hardenable by calcination to give sufficient cohesion and hardness to the agglomerate. The clays used are kaolinites, attapulgites, bentonites, halloysite or mixtures of these clays.

[015] It is also possible to use siliceous or aluminous binders. In particular, agglomeration with peptized aluminas gives very strong granules, this method of agglomeration being possible here because ferrierite is not degraded by the acidity of the binder.

[016] After agglomeration, the granules are thermally activated. This means that they are subjected to a calcination carried out under air at a temperature of approximately 400°C, the role of which is both to harden the binder, to dehydrate it without hydrothermally degrading it and, in the case of ferrierites exchanged starting from an ammonium form, to remove a large part of the ammonium ions and to bring the zeolite to the H form.

[017] It is also possible to start by agglomerating the sodium/potassium ferrierite, then to harden it by calcination and to carry out exchanges on the agglomerate. After drying, a second calcination makes it possible to bring the ferrierite/iron to the H form, if the ferrierite employed was taken in the ammonium form.

[018] This catalyst is the improved catalytic means of a process for destroying N₂O, contained in a gas mixture, according to the overall reaction:



[019] This process, which is also one of the subjects of the present invention, consists in passing the gases to be purified, in which the range of concentrations of N₂O extends from 500 ppm to 50%, of H₂O from 0.5 to 5% and of NO from 50 to 2000 ppm, through a catalyst bed placed in an axial or radial flow reactor maintained at a temperature of between 350 and 600°C. In the treatment of a gas with a high N₂O content and with an initial temperature of less than 350°C, as is generally the case in processes for organic synthesis by nitric oxidation, the initiation of the reaction can be facilitated by preheating, during the start-up phase, the gas flow or the catalyst by an external means, the temperature of the catalytic bed subsequently being self-supporting because of the exothermicity of the reaction. In certain situations, in particular in the

case of the treatment of gas with a high N_2O concentration, heat exchangers or devices of quench type can advantageously be immersed in the catalytic bed in order to control the temperature of the latter, it optionally being possible to use part of the heat to preheat the gas to be treated.

[020] Contrary to other zeolitic catalysts, the ferrierite/iron according to the invention retains a manifest activity with respect to N_2O in the presence of water. This activity is very much enhanced in the presence of NO, which is a very favorable factor because this synergy becomes more significant for very low levels of NO, of the order of 50 ppm, and because the gases capable of such a treatment almost always contain such traces of NO.

[021] The process according to the invention finds its application in particular in the treatment of tail gases from nitric acid plants, both before and after DeNO_x treatment, which gases can have compositions within the following limits,

- N_2O content: between 500 and 1500 ppmv,
- NO_x content: between 50 and 2000 ppmv,
- H_2O content: between 0.5 and 3%,
- oxygen content: approximately 2%,

the remainder being essentially composed of nitrogen.

[022] The process can also be applied to the treatment of gases resulting from plants for organic oxidation using nitric acid in organic chemistry, in particular in the manufacture of adipic acid, of glyoxal and of glyoxylic acid. These are gases with the approximate composition, before optional dilution with air, as follows:

- N_2O content: between 20 and 50%
- NO_x content: between 50 and 5000 ppmv,
- H_2O content: between 0.5 and 5%,
- oxygen content: between 1 and 4%,
- CO_2 content: approximately 5%,

the remainder being essentially composed of nitrogen.

EXAMPLES

[023] In the following examples, which are nonlimiting but intended to give a better understanding of the invention, the same catalytic test procedure has been followed, which procedure comprises the preparation of the sample and the catalytic test proper.

a) Preparation of the catalyst

[024] The exchanged zeolite powder is dried in an oven at 100°C and then mixed with a silica sol, containing 40% by weight of SiO₂, in an amount such that the silica SiO₂ content with respect to the SiO₂ + zeolite dry combination is 10%. The paste obtained is dried at 100°C for 6 hours and then reduced to a powder in a mortar. The powder is pelletized to pellets with a diameter of 5 mm which are activated in an oven at 400°C under air for 2 hours. After cooling, the pellets are crushed and sieved at 0.5 - 1 mm, this fraction constituting the catalyst.

b) Catalytic test

[025] It is carried out in a traversable stationary bed test unit (catatest) surrounded by heating shells regulated by PID, which brings the catalytic bed to a temperature approximately 25°C below their set-point temperature. The reactor has a diameter of 15 mm. The catalyst volume employed is 10 cm³, i.e. a bed with a height of 57 mm.

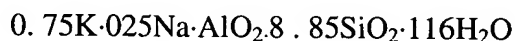
[026] The reaction gas is prepared from compressed air, from nitrogen and from standard gas, 2% N₂O in N₂, 2% NO in N₂. The water vapor content is adjusted by an air humidifier, according to the laws of vapor pressure.

[027] N₂O analyses are carried out by infrared and NO_x analyses by chemiluminescence.

[028] The results are expressed as degrees of conversion of N₂O to N₂.

EXAMPLE 1: Preparation of various ferrierite/iron compositions

[029] The ferrierite is supplied by Tosoh. Its Si/Al ratio is 8.85 and its Na and K-contents, on a dry basis, after calcination at 1000°C are 0.92% and 4.7% respectively. Taking into account its loss on ignition of 25% at 1000°C, its formula is



[030] The direct ferric exchange is carried out as follows. 100 g of zeolite powder are suspended, in a 1 liter round-bottomed glass flask, with 0.5 l of molar aqueous ferric chloride (FeCl_3) solution (i.e. 8.1 g of FeCl_3 per liter), namely with a volume of liquid/weight of dry solid ratio of 5. The system is kept stirred at 60°C for 4 hours. The exchanged zeolite is recovered by filtration on a filter funnel, washed by percolation with 2 liters of demineralized water at ambient temperature and then dried on a tray in a ventilated oven overnight.

[031] The iron, potassium and sodium contents with respect to the dry product (1000°C) are 2.7%, 2.8% and 0.16% respectively. These quantities can be varied by adjusting the temperature, the duration of the exchanges and their number.

Ref.	T°	Time (h)	Fe^{3+} exchanges	Fe %	Na %	K %
1.1	60	4	1	2.7	0.16	2.8
1.2	60	4	1	3.8	0.1	2.7
1.3	80	4	3	7.7	<0.05	0.16

[032] These products are subsequently named FERFe^{3+} Na, K form.

[033] The ferric exchange on ferrierite exchanged beforehand with ammonium ions is carried out as follows.

[034] A first exchange is carried out, on 100 g of the same zeolite as above, with 0.5 liter of an 800 g/l ammonium nitrate solution at a temperature of 80°C for 4 hours. The exchanged product is recovered, washed and dried as above. Its sodium content is less than 0.1% and its potassium content less than 0.15%.

[035] The ferric exchange is subsequently carried out as above but with two successive exchanges. The continuation of the operation is the same as in Example 1. A ferrierite/iron is obtained for which the iron, potassium and sodium contents are 2.2%, 0.15% and less than 0.1% respectively. These quantities can be varied by adjusting the temperature, the duration of the exchanges and their number. The following were thus obtained

Ref.	T°	Time (h)	Number of Fe ³⁺ exchanges	Fe %	Na %	K %
2.1	60	5	1	1.26		
2.2	60	4	2	2.2	<0.05	0.15
2.3	80	4	1	3.2	<0.05	0.12
2.4	80	4	2	7	<0.05	<0.05

[036] These products are subsequently named FERFe³⁺, NH₄ form.

EXAMPLE 2: Power of conversion of N₂O of ferrierites/iron³⁺ in gases with a low N₂O content

[037] The test is carried out, according to the experimental procedure explained above, on nitrogen enriched with

N₂O 1000 ppm

O₂ 2%

at an hourly volumetric rate or HVR of 10,000 h⁻¹.

[038] In addition, the gas may or may not contain nitrogen oxide NO or water. The specific conditions of the test are as follows

- 1: 375°C, NO = 0, H₂O = 0
- 2: 375°C, NO = 1000 ppm, H₂O = 0
- 3: 375°C, NO = 1000 ppm, H₂O = 3%
- 4: 400°C, NO = 1000 ppm, H₂O = 3%

[039] The following % conversion results are obtained

Conversion of N ₂ O to N ₂ , different conditions						
			Test conditions			
	Ref.	Fe %	1	2	3	4
Na, K form	1.1 -	2.7	10%	50%	30%	42%
	1.2	3.8	14	50	20	45
	1.3	7.7	35	75	34	72
H form	2.1	1.26	49	88	44	72
	2.2	2.2	46	97	48	77
	2.3	3.2	24	79	35	66
	2.4	7	33	84	52	85

[040] An excellent activity of the ferrierite /iron, H form, is observed.

EXAMPLE 3: Power of conversion of N₂O of ferrierites /iron²⁺ in gases with a low N₂O content

[041] The preceding operations are repeated but, instead of ferric chloride, the exchange is carried out with a ferrous salt, ferrous sulphate FeSO₄ 7H₂O. The procedures are carried out equally in Na, K form and in NH₄ form. The products of the FERFe²⁺, Na, K form, series:

Ref.	T°	Time (h)	Number of Fe ²⁺ exchanges	Fe %	Na %	K %
3.1.1	80	4	1	1.8	0.25	3.2
3.1.2	80	4	3	4.1	0.2	1.8

and the products of the FERFe²⁺, NH₄ form, series:

Ref.	T°	Time (h)	Number of Fe ²⁺ exchanges	Fe %	Na %	K %
3.2.1	80	4	1	1.7	<0.05	0.15
3.2.2	80	4	3	5.46	<0.05	0.15

are thus obtained.

[042] The results of the catalytic test are as follows, the conditions being those in the preceding example:

Conversion of N ₂ O to N ₂						
			Test conditions			
	Ref.	Fe %	1	2	3	4
Na, K form	3.1.1	1.8	12%	90%	22%	43%
H form	3.2.1	1.7	31	93	48	78
	3.2.2	5.46	29	98	50	78

[043] An excellent activity of the ferrierite/iron, form H, is observed. There is no substantial difference between the ferric and ferrous series.

EXAMPLE 4: Conversion of N₂O – comparison of various zeolites/iron

[044] Various zeolites/iron, all exchanged in their NH₄ form starting from ferrous sulphate, are now compared with a ferrierite/iron²⁺, at iron assays in the region of 2%. The zeolite Y is a Y with an Si/Al ratio of 20 and assays, after exchange, 1.8% of iron and < 0.1% of sodium; the pentasil has an Si/Al of 13.5 and assays, after exchange, 1.6% of iron and < 0.05% of sodium; the beta has an Si/Al of 12.5 and assays, after exchange, 1.9% of iron and < 0.05% of sodium; the mordenite has an Si/Al of 5.5 and assays, after exchange, 1.9% of iron and < 0.05% of sodium. The ferrierite is the ferrierite with the reference 2.2 in Example 2.

Conversion of N ₂ O					
Zeolite	Iron %	Test conditions			
		1	2	3	4
Y	1.8	28	45	22	38
Pentasil	1.6	7	62	14	30
Beta	1.9	47	98	21	44
Mordenite	2.4	8	91	22	42
Ferrierite	2.2	46	97	48	77

[045] It is found that only the ferrierite retains a significant activity in conversion of N_2O in the presence of water vapor.

EXAMPLE 5: Comparative activities of a mordenite/iron and of a ferrierite/iron in gases with a high N_2O content

[046] The reduction in the N_2O content obtained with the preceding mordenite/iron containing 2.4% of iron is compared with that of two ferrierites, one containing 1.46% of iron and the other containing 3.37% of iron.

[047] The conditions of the test are

N_2O	5%
O_2	5%
HVR	$10,000\ h^{-1}$
5:	$325^\circ C$, NO = 0
6:	$325^\circ C$, NO = 1000 ppm
7:	$375^\circ C$, NO = 0
8:	$375^\circ C$, NO = 1000 ppm
9:	$425^\circ C$, NO = 0
10:	$425^\circ C$, NO = 1000 ppm
11:	$475^\circ C$, NO = 0
12:	$475^\circ C$, NO = 1000 ppm

[048] The degrees of decomposition below are recorded.

Conversion of N_2O to N_2									
	Fe %	Test conditions							
		5	6	7	8	9	10	11	12
Mordenite/iron	2.4	0.1	0	0.8	14.3	6.8	21.6	35.2	65.8
Ferrierite/iron	1.46	1.6	1.2	5.3	11.6	12.3	36.7	42.1	8.7
Ferrierite/iron	3.37	0.8	3.2	1.1	13.2	5	93.4	49.3	99.9

[049] These results exhibit a higher level of conversion of N_2O with the ferrierite.

EXAMPLE 6: Aging

[050] The result of a comparative hydrothermal stability test between a mordenite/iron with an Si/Al ratio of 5.5, H form, exchanged with iron to the level of 2.4% by weight, and a ferrierite/iron according to the invention, an H form, exchanged with iron to the level of 2.2% (reference 2.2 in Example 1), is reported here.

[051] The aging was carried out by exposure of the catalysts to an air/water vapor mixture in a dried bed at 650°C for 3 hours. The air is saturated with water vapor at 90°C.

[052] The two catalysts are, tested as above with respect to conversion of N₂O, the operating conditions being

N₂O 1000 ppm

NO 1000 ppm

O₂ 10%

Temperature: 375°C

HVR 10,000 h⁻¹

13: H₂O = 0

14: H₂O = 3%

[053] The following results are obtained:

Conversion of N ₂ O to N ₂			
		Test conditions	
		13	14
Mordenite	Before aging	91	22
Mordenite	After aging	32	10
Ferrierite	Before aging	88	40
Ferrierite	After aging	83	39

which results confirm the remarkable stability of the ferrierite/iron to water vapor.

EXAMPLE 7: Granules with an aluminous binder

[054] In a first step, extrudates containing 20% of aluminous binder are formed as follows. An alumina of NG type, supplied by the company Condea, is used for the manufacture of the agglomerated catalyst. In a first step, it is peptized by continuously introducing, into a mixer,

alumina at the rate of 15 kg/h and 5% by weight nitric acid with a flow rate of 0.16 l/min. 5 kg of the peptized alumina gel thus obtained are mixed with 10 kg of ferrierite powder, in the Na, K form, as supplied by Tosoh (see Example 1), in a conventional powder mixer. The resulting mixture is fed to a mixer/extruder at the same time as 3 liters of water. The extruder is a device of Redco type from the company Aoustin, with a diameter of 5 cm, equipped at the outlet with a die forming extrudates with a diameter of 3.8 mm which are cut into elements with a length of 5 to 10 mm. The extrudates are subsequently transferred, with a thickness of approximately 15 mm, to a muffle furnace, through which air passes, at 100°C for 4 hours and then at 450°C for 3 hours, in order to confer a satisfactory mechanical strength on them.

[055] 200 g of these ferrierite extrudates are now introduced into a stainless steel basket in order to steep them in 1 liter of an 800 g/l ammonium nitrate solution at a temperature of 80°C for 3 hours, then to wash them by successive steepings (3) in 1 liter of demineralized water, and then to dry them at 100°C.

[056] Their sodium and potassium content on a dry basis (1000°C) is 0.1% (Na) and 0.15% (K).

[057] Exchange with iron is then carried out according to the same principle with 1 liter of iron (Fe^{2+} sulphate solution containing 280 g/l of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at 80°C for 3 hours, followed by washing by successive steepings in 1 liter of demineralized water and by drying. The iron content on a dry basis (1000°C) is 1.6%.

[058] The catalyst thus prepared is subjected to the catalytic test described above in a reactor with a diameter of 25 mm. The catalyst volume is 25 cm³, i.e. a height of approximately 5 cm. The catalytic test is applied under the conditions 1 to 4 of Example 2.

[059] The following are obtained:

Conversion of N_2O to N_2				
Catalyst	Test Conditions			
	1	2	3	4
Aluminous granules	30%	89%	43%	72%

which are results highly comparable with those of Example 2.1.